# Comparison of $CO_2$-Sources for Fuel Synthesis

## T. WEIMER, K. SCHABER

Institut fuer Technische Thermodynamik und Kaeltetechnik University of Karlsruhe, Germany;

## M. SPECHT, A. BANDI

Center for Solar Energy and Hydrogen Research, Stuttgart, Germany

## 1    Strategies for the Substitution of Fossil Fuels

As it has been estimated in several publications, e.g. [3], the combustion of fossil fuels contribute with about 50 % to the global warming due to the increasing concentration of atmospheric $CO_2$. Short term strategies for the reduction of the $CO_2$-emissions are energy saving and efficient utilization. But as a successful long term strategy to stabilize the atmospheric $CO_2$-content only the substitution of fossil fuels by renewable energy sources can be accepted. The potential of renewable energy sources is by several magnitudes higher than any estimated future world energy demand, [7]. Unfortunately, large renewable energy sources are almost located far away of the main energy consumption areas, e. g. in desert regions, mountains or over the oceans. If there is no realistic possibility to join an electric grid, renewable energy must be transported by energy carriers. For the intercontinental transport of energy as well as for energy storage, the generation of chemical energy carriers is the best alternative. Possible alternatives are hydrogen or liquid carbonaceous energy carriers.

On the other hand, mobile applications of carbonaceous fuels have the most dynamic growth of all energy consumption sectors. Here chemical energy carriers are again the best alternative for the storage of energy on board. Both, hydrogen and methanol generated from renewable energy sources can be applied as energy carrier in automobiles. In opposite to fossil fuels, they open the possibility to use high efficient fuel cells in transport applications. Even automobiles with high efficient combustion engines consume about the double amount of energy per mileage then fuel cell equipped cars. Therefore in mobile applications as well as for electricity the renewable generated energy carrier can substitute about the double of fossil primary energy. The most likely choice for the large scale substitution of fossil energy carriers is the generation of electricity from renewable energy or fuels for mobile applications with remote renewable energy sources.

## 2    Renewable Fuels for Mobile Applications

For the generation of a climate neutral fuel using renewable energy, a closed loop process without net emissions is necessary. The generation of hydrogen from water achieves the monoxide shift reaction is shown in figure 1. With the $CO_2$ recovery and compression to 60 bar a reduction of the energetic efficiency of the power station to 38,1 % from 43,6 % without $CO_2$ recovery was estimated. 88 % of the $CO_2$ emissions are recovered For simplifying the further discussion pure Carbon with a heating value of 393 kJ/Mol is assumed as energy source. In the basic case without $CO_2$ recovery we achieve an electric output of 171 kJ(el)/Mol Carbon leading to a specific $CO_2$ emission of 5,85 Mol $CO_2$/MJ(el). To achieve this electrical output of 171 kJ(el) in the process including a $CO_2$ recovery unit, 1,14 Mol of Carbon have to be fired at the new efficiency of 38,1 %. $CO_2$ recovery of 88 % leads to 1,14*0,88=1 Mol $CO_2$/171 kJ(el) and $CO_2$ emissions of 0,14 Mol $CO_2$/171 kJ(el) equivalent to 0,82 Mol $CO_2$/MJ(el). The additional fossil energy demand $E_{Carbon}$ for the recovery of the 1 Mol $CO_2$ is 0,14 Mol carbon with a heating value of 393 kJ/Mol, leading to:

$$E_{Carbon} = 55 kJ/Mol\, CO_2 . \tag{1}$$

A compression of $CO_2$ to 60 bar is included in the energy demand. The energy demand for drying and liquefaction of the compressed $CO_2$ is neglected.

Power plants fired with Natural Gas have lower specific emissions of $CO_2$. A power plant fired with Natural Gas can achieve specific $CO_2$ emissions of only 2,3 Mol $CO_2$/MJ(el) without any $CO_2$ recovery process. Because of the lower partial pressure of $CO_2$ in the flue gas compared to the resulting partial pressure of coal gasification a chemical absorption process with MEA Solutions leads to the lowest specific energy demand for $CO_2$ recovery

1337

in natural gas fired power plants. This process was investigated by Suda et. al., [5]. Suda achieved in a pilot plant a steam demand of about 170 kJ/Mol $CO_2$ and an electric energy demand of 2,6 kJ/Mol $CO_2$. Unfortunately, the power plant efficiency without $CO_2$ recovery was not published by Suda et. al. The fossil energy demand for the $CO_2$ recovery should be in the range of 180 kJ/Mol $CO_2$ assuming high efficiencies for steam and electricity generation. For the utilization in a distant located fuel synthesis, the $CO_2$ has to be dried, compressed and liquefied for transportation. Taking the estimated energy demand of Hendriks [1] for compression, additional 10 kJ(el)/Mol $CO_2$ are required, leading to a total fossil energy demand $E_{NG}$ of

$$E_{NG} = 200 kJ/Mol CO_2 . \tag{2}$$

The drying and liquefaction are again neglected in the estimated energy demand. The $CO_2$ recovery process reduces the specific $CO_2$ emissions to the very low value of 0,3 Mol $CO_2$/MJ(el).

In existing facilities of the lime and cement industry the carbon dioxide content in the flue gas is about 60 % at atmospheric pressure. A promising alternative for $CO_2$ recovery is flue gas compression before a physical absorption process to avoid thermal regeneration of the scrubbing liquid. The compression of the flue gas from atmospheric pressure up to 10 bar at a temperature of 330 K and of the recovered $CO_2$ up to 60 bar from atmospheric pressure lead to a resulting electric energy demand of about 25 kJ/Mol $CO_2$. With an energetic efficiency in the range between 40 and 50 % for the generation of electricity the fossil energy demand for $CO_2$ recovery in the lime and cement industry is in the same range (50-60 kJ/Mol $CO_2$ ) as for the $CO_2$ recovery process in coal fired power plants.

The utilization of $CO_2$ from concentrated emissions for fuel synthesis at remote renewable energy sources leads independent of the kind of source to a long distant transport of the recovered $CO_2$. For this purpose $CO_2$ has to be liquefied and transported. The $CO_2$ must be dried before liquefaction, for example by absorption with triethylene-glycol, and cooling water at temperatures below 293 K is required for the liquefaction. At least special transport facilities are necessary.

## 3.2 Enrichment of $CO_2$ from Atmosphere

A process for the recovery of $CO_2$ from the atmosphere can be located anywhere. Two process designs, based on absorption of $CO_2$ in caustic solutions, have been estimated, [7]. Taking solar energy as energy input, a process with precipitation of limestone from the scrubbing solution is more attractive than a regeneration of the scrubbing solution by electrodialysis, which is an interesting alternative if wind or hydro power are the energy sources. The basic design of the solar energy $CO_2$ recovery process is shown in figure 2. An electric energy demand of 70 kJ/Mol $CO_2$ and a heat demand of 250 kJ/Mol $CO_2$ was estimated, [7]. Investigations show that an electric energy demand of about 40 kJ/Mol $CO_2$ is achievable for the absorption process. Optimization of the precipitation can minimize the thermal energy demand for limestone decomposition to about 200 kJ/Mol $CO_2$, similar to the energy demand in the limestone industry for the thermal decomposition process. Solar efficiencies of 0,2 for the generation of electricity and 0,7 for heat generation lead to a solar energy demand $E_{Solar}$ of

$$E_{Solar} = 500 kJ/Mol \quad CO_2 . \tag{3}$$

The recovered $CO_2$ can be processed directly without transportation or storage. Drying is not necessary. Additionally, because the $CO_2$ is produced at temperatures of about 1200 K, solar high temperature processes like a conversion to carbon monoxide with hydrogen can be attached to the recovery process. A disadvantage is the need for absorption columns with huge diameters to process the air with a low $CO_2$ content of 0,035 %. As the required packing height is only three to five meters and low cost concrete can be used for the column, the investment costs should be moderate. Nevertheless, additional investigations for secure uniform fluid flows in the absorption column at energy optimized conditions with low pressure drop are necessary.

## 3.3 Comparison of Renewable and Fossil Energy Demand

A direct comparison of the fossil energy demands (1), (2) with the renewable energy demand (3) shows a much greater energy demand for the $CO_2$ recovery from the atmosphere compared to concentrated emissions. But the fossil energy demand for $CO_2$ recovery is consumed at locations with a high energy demand and could be directly used in different

alternative manners. The renewable energy source, if used for $CO_2$ enrichment and fuel synthesis instead of electricity generation will be located remote.

The only alternative utilization of the renewable energy used for the $CO_2$ enrichment from the atmosphere is supplying the fuel synthesis. A solar efficiency for the generation of methanol (MeOH) using atmospheric $CO_2$ of 0,136 has been estimated [7]. Neglecting the energy demand for the $CO_2$ enrichment and all losses during transport of $CO_2$ and methanol a very high solar efficiency of 0,16 for the generation of methanol can be assumed. With the renewable energy demand (3) of 500 kJ/Mol $CO_2$ for the enrichment of 1 Mol $CO_2$ from the atmosphere an alternative synthesis of only 80 kJ MeOH is possible. Assuming application in fuel cell equipped cars, these 80 kJ MeOH can substitute the double amount of gasoline. Instead of the enrichment of 1 Mol $CO_2$ from the atmosphere with 500 kJ solar energy the substitution of 160 kJ gasoline with the aid of these 500 kJ renewable energy is therefore possible under optimistic assumptions.

The comparison of the possible fossil energy substitution

$$E_{subs} = 160 kJ/Mol \quad CO_2 \tag{4}$$

resulting from the solar energy demand (3) with the fossil energy demand (1), (2) leads to a more realistic energetic estimation for a decision between the different $CO_2$ sources for climate neutral fuel synthesis.

# 4    Comparison of the $CO_2$ Sources

The most efficient recovery processes of $CO_2$ from concentrated emissions achieve an optimistic energy demand of about 50 kJ/Mol $CO_2$ (1) obtaining gaseous $CO_2$ at 60 bar pressure. The costs per ton $CO_2$ recovered are estimated by [1] to 25 DM/t. But here the costs for drying, liquefaction, storage and transportation are not included. For the intercontinental transport tank ships will be employed. Because at ambient temperatures huge high pressure tanks at 60 bar would be required, low temperature transport at temperatures of 200 K at ambient pressure will be preferred because of lower costs. This causes investment for well isolated tank ships with cooling of the $CO_2$ during transport. An alternative is to cool the $CO_2$ by evaporation with resulting $CO_2$ losses.

The $CO_2$ recovery from the atmosphere will achieve an equivalent fossil energy demand of less than 160 kJ/Mol $CO_2$ (4). The only investment are for the absorption column and for the solar heated drying and thermal decomposition of limestone. No infrastructure for transport and storage of $CO_2$ is necessary. A combination of the $CO_2$ recovery from air with other solar high temperature processes is possible increasing the efficiency for the fuel generation process. This will reduce the energy demand for the methanol synthesis with atmospheric carbon dioxide as basic product. If this process is optimized, an energetic and economic comparison of the whole methanol synthesis process with renewable energy and different $CO_2$ sources will show the most promising $CO_2$ source.

Although further investigations and development are still necessary, the $CO_2$ recovery from air seems to be the better alternative compared to the $CO_2$ recovery from concentrated emissions even from today's state of investigation. The higher energy demand is supplied by remote located climate neutral energy. But the savings in investment costs compared to the utilization of concentrated $CO_2$ sources needing a complex infrastructure can be taken for the extension of the renewable energy plant. The more extensive use of renewable energy can supply the energy demand for the $CO_2$ enrichment from air.

# References

[1] C.A. Hendriks, K. Blok, and W.C. Turkenburg. *Energy*, 16:1277, 1991.

[2] IEA. Carbon dioxide capture from power stations. Technical report, International Energy Agency, 1994.

[3] Enquetekomission des dt. Bundestags Schutz der Erdatmosphaere. *Mehr Zukunft fuer die Erde.* Economica Verlag, Bonn, 1995.

[4] M. Steinberg and A.S. Albanese. BNL 50877: Environmental control technology for atmospheric carbon dioxide. Technical report, Brookhaven National Laboratory, Upton NY, 1978.

[5] T. Suda, M. Fujii, and K. Yoshida. *Energy Conv. Mgmt.*, 33:317, 1992.

[6] Various. In *Proceedings of the 2nd International Conference on $CO_2$ Removal*, Kyoto, 1994.

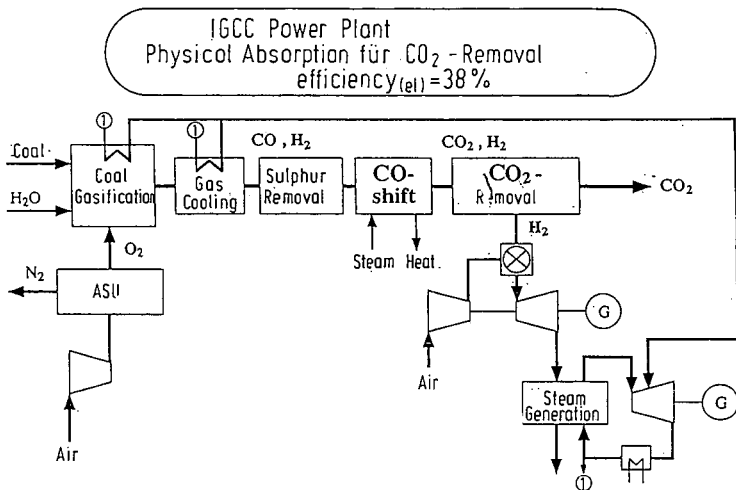[7] T. Weimer, K. Schaber, and et al. *Energy Conv. Mgmt.*, 37(6-8):1351–1356, 1996.

Figure 1: Coal fired Integrated Gasification Combined Cycle (IGCC) process for generation of electricity with $CO_2$ recovery and compression to 60 bar
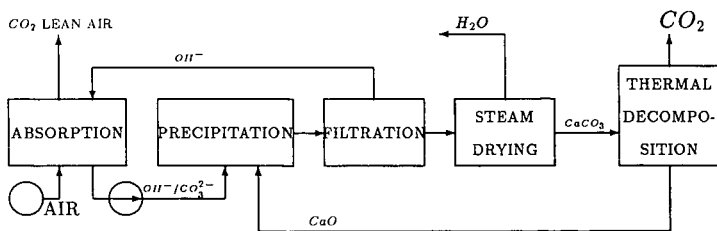


Figure 2: $CO_2$-Recovery from Air with Precipitation of Limestone